91600
new 82-10

COMPLIMENTARY COPY
Please Credit Ontario Hydro Research if
Reproduced in Whole or in Part.

ontario hydro
research division

To Mr. F.J. Kee
Director of Research

IMPROVED DICHOTOMOUS-SAMPLER FILTER ANALYSIS

O. Herrmann

The analysis of dichotomous-sampler filters, used for atmospheric pollution monitoring, has been substantially improved. Detection limits for particulate ammonium, sulphate and nitrate species have been reduced from 2, 9.6 and 12 µg/filter to 1, 3 and 1 µg/filter, respectively. Detection limits of gaseous species have been reduced from 13 and 4.8 µg/filter to 10 and 1 µg/filter for sulphate and nitrate, respectively. These improvements were achieved by changes in methodology as well as changes in sample handling which served to reduce the blanks and the variations in the blanks. In spite of increased sample handling, the efficiency of the analytical procedure has been improved to reduce the cost to about 75% of the original method cost.

1.0 INTRODUCTION

A previous report/1/ described a dichotomous-sampler system and the extraction and continuous-flow analysis methods for the determination of sulphate, nitrate and ammonium species in filters from this system. These methods were shown to give results comparable to those obtained by the accepted ion-chromatographic method but at a significantly lower cost and higher sample throughout. A trial period of several months showed that a significant number of samples contained analyte concentrations below the detection limits of the existing system, especially for nitrate. The Atmospheric Research Section requested that the methods be reviewed in order to retrieve more data from the testing program and to more closely match the detection limits of other agencies such as the Ontario Ministry of the Environment. A lowering of the detection limits by about an order of magnitude was considered desirable.

job	file	date	report no.
740635-526-036	837.201	December 15, 1982	82-521-K

The original detection limits were considered to be limited by the blanks and by variations in these blanks. This report describes the steps taken to identify the sources of these blanks and attempts to reduce their influence. Some procedural changes were also required to improve the sensitivity of the sulphate determination.

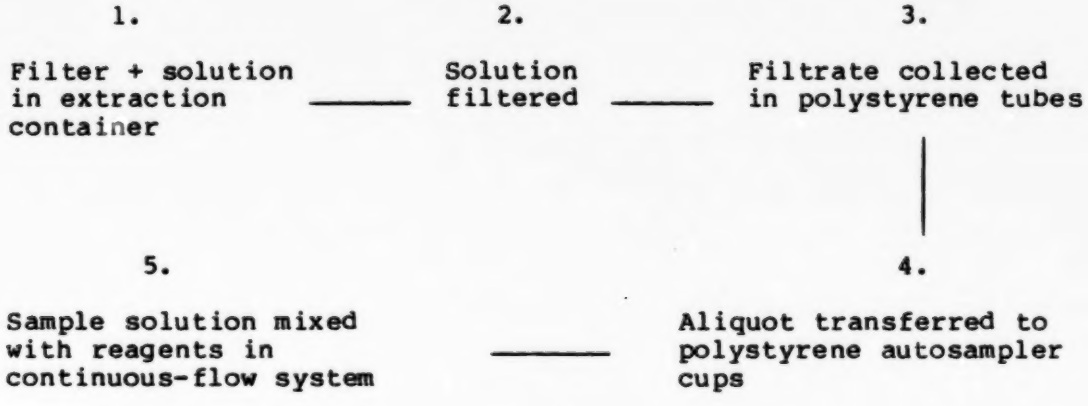
2.0 DICHOTOMOUS SAMPLING SYSTEM

Dichotomous samplers were initially designed to collect atmospheric particulates. The atmospheric Research Section expanded their scope to obtain information on gaseous species as well. In this expanded system, sampled air is split into two streams. The first stream contains coarse particulates and is filtered through a teflon filter. The second stream is directed through a pack of three filters to collect different fractions of the air stream. The upper teflon filter collects fine particulates. Both the coarse and fine particulates are analyzed for ammonium, sulphate and nitrate species. The second filter in the filter pack is nylon and is designed to collect gaseous nitrate species. The third, and bottom filter is cellulose impregnated with potassium carbonate in order to trap sulphur dioxide from the air stream.

The filters are used for a 24-hour sampling period and then returned to the Atmospheric Research Section. The filter packs are separated and the filters individually sealed in plastic petri dishes before being transferred to the Analytical Service Section. Unused filters are carried through the analytical procedure to provide blanks. These blanks are used to study changes in the analytical procedure but are not used in the analysis of real samples. A more rigorous procedure is used to provide a better estimate of the total blank resulting from handling. Unused filters are carried to the sampling site then returned along with regularly used filters. These are referred to as "field" blanks to distinguish them from new unused filters obtained directly from the manufacturer.

3.0 ANALYTICAL PROCEDURE

When they are received in the laboratory, the filters are transferred to extraction containers and extracted with 20 mL of extractant in an ultrasonic bath. The efficacy of this method was described in a previous report/2/. The extract is filtered to remove insoluble species then analyzed by continuous-flow analysis procedures based on colorimetric methods/3,4/. The steps involved in the procedure are shown below.



Each stage of the analytical procedure can be a significant source of contamination. The major portion of this report describes the investigation of contamination sources and the attempts to minimize their effect. In the case of sulphate determinations, some modifications were also required in the continuous-flow system itself in order to improve detection limits.

Except where otherwise specified, all results given are based on continuous-flow analysis.

4.0 RESULTS AND DISCUSSION

4.1 Effect of Extraction Containers

In the interim between the original report/1/ and the present study, some steps had already been taken to reduce the observed blanks. The linear polyethylene (LPE) extraction bottles which were initially used were discovered to exhibit notable memory effects despite rigorous cleaning procedures. This memory effect resulted in occasionally substantial variations in the blanks and in sample results due to contamination between batches. The use of disposable glass vials was found to be the most suitable alternative. The vials were acceptable for use after an initial wash with deionized water.

Table I shows that some improvement was obtained, especially for nitrates on nylon filters, but that a high degree of variability remained. In addition to this improvement, total costs were lower with the use of glass vials because much more extensive cleaning was required for LPE bottles.

TABLE I

EFFECT OF EXTRACTION CONTAINER ON BLANKS

		TEFLON			NYLON			IMPREGNATED		
	Analyte	Blank µg/filter	Std Dev µg/filter	N	Blank µg/filter	Std Dev µg/filter	N	Blank µg/filter	Std Dev µg/filter	N
LPE Bottles Sample Batch	SO_4^{2-}	1.0	4.5	26	6.0	2.4	23	30	6.5	20
	NO_3^-	8.6	6.0	26						
	NH_4^+	0.2	1.0	26						
Glass Vials Jan 18/82	SO_4^{2-}	-0.7	5.5	24	2.3	1.0	7	22	3.5	7
	NO_3^-	4.0	2.5	24						
	NH_4^+	-1.1	0.5	24						
Glass Vials Feb 2/82	SO_4^{2-}	-0.8	5.0	20	2.2	1.5	10	19	4.5	10
	NO_3^-	7.1	6.0	20						
	NH_4^+	-0.8	0.9	20						
Glass Vials March 10/82	SO_4^{2-}	0.8	5.5	18	1.2	1.5	9	16	6.5	9
	NO_3^-	1.3	0.5	18						
	NH_4^+	-1.2	0.4	18						

(i) N = number of samples in batch
(ii) Negative values arise from noise and baseline drift.

4.2 Contamination From Other Sources

Although some improvements were noted in the blanks as a result of changing extraction containers, a more detailed study of contamination sources was required. Details of the investigation are provided for teflon filters and are subdivided according to analyte. Similar methods were used to investigate the nylon filters and thus only a summary of results is provided. No major changes were made in the handling of the impregnated filters because a major source of contamination was the impregnating

material itself and analyte levels were generally significantly higher than the detection limit.

4.2.1 Nitrate on Teflon Filters

4.2.1.1 Comparison of Continuous-Flow Analysis and Ion Chromatography

Water alone as well as three batches of new teflon filters were carried through the entire analytical process up to the final determination. Nitrate concentrations were determined for each sample by both ion chromatography and continuous flow analysis. The results are given in Table II.

TABLE II

METHOD COMPARISON

Sample	Continuous-Flow Analysis			Ion Chromatography		
	Nitrate µg/filter	Std. Dev. µg/filter	N	Nitrate µg/filter	Std. Dev. µg/filter	N
20 mL deionized water carried through process	1.39	0.31	10	1.19	0.35	10
20 mL deionized water + lot 1470 filter	1.60	0.38	8	0.96	0.17	8
20 mL deionized water + lot 1915 filter	0.82	0.21	10	0.67	0.18	10
20 mL deionized water + lot 1920 filter	1.55	1.24	10	0.90	0.15	10

N = Number of samples in a run.

The difference between batches of filters or between methods of analysis was not statistically significant. This indicated that no advantage would be obtained by the use of ion chromatography

with the present system. Therefore, lower limits of detection obtained by other laboratories using ion chromatography must be due to different sampling methods and lower levels of contamination.

4.2.1.2 Sources of Contamination

Sources of contamination were examined by analyzing deionized water taken from different stages of the analytical procedure. All determinations were carried out by continuous-flow analysis. Results are shown in Table III.

TABLE III

CONTAMINATION IN PROCESSING TEFLON FILTERS

Sample Process Steps	Nitrate µg/filter	Std. Dev. µg/filter	No. of Samples
1. Water from glass vials which had been rinsed once.	0.140	0.093	10
2. Water from glass vials which had been rinsed five times.	-0.013	0.077	10
3. Water added directly to autosampler cups.	-0.125	0.056	10
4. Water added to polystyrene tubes then transferred to autosampler cups.	0.435	0.095	10
5. Water added directly to autosampler cups.	0.058	0.010	10
6. Piltrate from filtration apparatus.	1.280	0.337	12
7. Water carried through entire process.	1.392	0.312	10
8. Water added directly to autosampler cup.	-0.165	0.011	8
9. Filtrate from filtration apparatus analyzed with in-line ion exchanger.	1.360	0.346	12
10. Water added directly to autosampler cup analyzed with in-line ion exchanger.	-0.007	0.013	8

All analyses involved addition of sample to autosampler cups prior to actual analysis. In order to ensure that observed effects were not due to variable contamination from this source, each stage of the investigation involved a separate run of samples of water added directly to the cups (Step 3, 5, 8 and 10 in Table III). Contamination from this source was generally small and constant, although the sample standard deviation was considerably increased in Step 3. The glass extraction vials were also observed to be relatively contamination-free even after only one rinse. The polystyrene filtrate collection tubes were a significant source of contamination and blank variation but the filtration apparatus itself was found to be by far the greatest contamination source. In order to check whether this was a case of direct contamination or positive interference caused by metal ions which might react with the colour reagent, an in-line cation exchange column was added to the continuous-flow system. Steps 9 and 10 show that no improvement was obtained, suggesting the occurrence of direct contamination.

The filtration apparatus used is a 12-port system (12 samples are filtered simultaneously through separate holes in the top of the apparatus) which normally requires a single large filter (0.45 µm pore size). Only one type of filter is commercially available for this system and the filter material was subsequently discovered to be a mixture of cellulose acetate and cellulose nitrate. Although the filter is always washed before use, it is hardly surprising that it contains leachable nitrates. Although less convenient, it is possible to use a separate conventional small filter for each port, thereby providing a choice of alternative materials. The filtration apparatus was tested with various filters. Results are given in Table IV below.

TABLE IV

EVALUATION OF FILTRATION SYSTEM

Sample Process Steps	Nitrate µg/filter	Std. Dev. µg/filter	No. of Samples
1. Water added directly to polystyrene collection tube.	0.607	0.072	6
2. Filter port rinsed and water collected in tube.	0.611	0.044	6
3. Water filtered through cellulose acetate-nitrate filter.	1.087	0.197	6
4. Water filtered through cellulose acetate-nitrate filter which was soaked in 0.1 N HCl overnight.	0.616	0.077	6
5. Water filtered through 0.6 µm pore PVC filter.	0.557	0.095	6
6. Water filtered through 0.45 µm pore cellulose acetate filter.	0.074	0.170	12

Cellulose acetate filters were chosen for subsequent use based on these tests.

Another source of blank variability was considered to be due to the colorimetric determination method itself. In this continuous flow system, nitrate is actually reduced to nitrite which is then reacted to produce a coloured species. Thus the method actually determines nitrate plus nitrite although results are normally reported as total "nitrate" species. Ion chromatography, however, separates these species and only nitrate is determined. At the higher nitrate concentrations previously examined, the nitrite concentrations were comparatively low and no correlation was observed between nitrate and nitrite levels. With an improvement in detection limits, much lower levels of nitrate are measured and the contribution of nitrite becomes significant. The contribution of nitrite to the variance of the

nitrate concentration also becomes significant at lower concentrations. Thus in subsequent runs, nitrate plus nitrite were determined with the reduction column in place as usual and nitrite alone was determined by removing the reduction column. The factor used to correct for the presence of nitrite must be determined by running nitrite standards through the column rather than using a theoretically calculated factor.

The system was tested by running water, three lots of new filters (same lot as shown in Table II) and one lot of field blanks. Results are provided in Table V.

TABLE V

NITRATE AND NITRITE BLANKS ON TEFLON FILTERS

Sample	N	Nitrate µg/filter	Std. Dev. µg/filter	Nitrite µg/filter	Std. Dev. µg/filter
1. Water taken through process	3	0.18	0.14	0.17	0.11
2. Water + Lot 1470 filter.	10	0.65	0.45	0.70	0.82
3. Water + Lot 1915 filter.	10	0.44	0.37	0.27	0.36
4. Water + Lot 1920 filter.	10	0.39	0.30	0.34	0.55
5. Water + Aug 19/82 field blank filter	5	0.40	0.43	0.45	0.65
6. Water + Sep 24/82 field blank filter	20	0.98	0.70	0.57	0.45

(i) n = number of samples
(ii) nitrate values corrected for nitrite

No significant difference is seen between lots or between new filters and field blanks. Both the sample standard deviations and the absolute values of the blanks are reduced compared to those obtained at the beginning of the present study. Thus the detection limit (defined as twice the sample standard deviation)

for nitrate on teflon filters is currently about 1 µg/filter compared to the original/1/ value of 12 µg/filter.

Similarly, the changes in extraction containers, filters and improved handling has reduced the detection limit for ammonium ions from 2 µg/filter to 1 µg/filter.

4.2.2 Sulphate on Teflon Filters

Changes in extraction containers and filtration apparatus were not sufficient to improve detection limits to desired levels. The analysis of several thousand teflon filters showed that over 95% of them contain less than 150 µg sulphate per filter. The original analytical range of 0 to 600 µg/filter was therefore unnecessarily broad and resulted in inferior values at low concentrations. The existing set-up lacked the required sensitivity and the spectrophotometer response was too noisy to allow scale expansion. Thus, in addition to reducing contamination, a number of changes were required in the system.

1. The spectrophotometer flow cell was changed from 2 mm diameter x 15 mm length to 2 mm diameter x 50 mm length. The longer path length improved the signal-to-noise ratio because of the larger absorbance change per concentration unit and by a greater averaging of the noise caused by particulates in the sample stream.

2. Full damping was used instead of zero damping in order to reduce noise.

3. The sampling rate of the continuous-flow analyzer was changed from 45 to 35 per hour and the sample-to-wash ratio was changed from 6:1 to 2:1. Both these measures serve to reduce carry-over from one sample to the next (intersample contamination), resulting in improved accuracy at low concentrations (especially if the first sample is relatively concentrated).

4. The in-line ion exchange column (used to reduce interference) was increased in size to ensure complete exchange during sample passage and to guarantee adequate capacity for an entire run.

A final test of the new system yielded the results given in Table VI.

TABLE VI

SULPHATE ON TEFLON FILTERS

Sample	n	Sulphate µg/filter	Std. Dev. µg/filter
1. Deionized water added to autosampler cups.	10	-4.6	1.6
2. Deionized water carried through complete extraction.	4	2.7	1.2
3. New teflon filter carried through extraction.	20	1.4	1.1
4. Field blank, run #1.	8	-2.2	1.8
5. Field blank, run #2.	8	1.9	0.8
6. 10 µg/filter sulphate standard carried through process	10	8.7	2.0
7. 50 µg/filter sulphate standard carried through process.	10	47.9	1.0

(i) n = number of samples in run
(ii) negative recorded values arise from noise and baseline drift

4.2.3 Nitrate on Nylon Filters

The nylon filters were examined for nitrate contamination similarly to the teflon filters. Results are summarized in Tables VII and VIII.

TABLE VII

CONTAMINATION IN NYLON FILTER PROCESSING

Sample	n	Nitrate µg/filter	Std. Dev. µg/filter
1. NaOH extractant added to auto-sampler cup.	5	0.13	0.04
2. NaOH added to polystyrene tubes then transferred to autosampler cup.	10 6	0.38 0.50	0.11 0.06
3. Empty filter port washed with NaOH. Wash collected in polystyrene tube and transferred to autosampler cup.	6	0.45	0.07
4. Sample as in 3 but cellulose acetate-nitrate filter used.	6	0.85	0.23
5. Sample as in 4. Filter soaked overnight in 0.1 M hydrochloric acid.	6	0.52	0.07
6. Sample as in 4. PVC filter (0.6 µm pore).	6	0.78	0.37
7. NaOH carried through complete process using cellulose acetate-nitrate filters in port.	10	1.25	0.92
8. Lot 2075 nylon carried through extraction.	10	1.74	0.63
9. Lot 2125 nylon carried through extraction.	10	2.31	0.74
10. June 24/82 field blanks.	10	1.97	0.94
11. July 16/82 field blanks.	10	2.59	0.55

(i) n = number of samples
(ii) nitrate values are for "total" nitrate (nitrate + nitrite).

Blanks were reexamined after instituting the changes in processing as outlined in Section 4.2.1.2.

TABLE VIII

NITRATE AND NITRITE BLANKS OF NYLON FILTERS

	Sample	n	Nitrate µg/filter	Std. Dev. µg/filter	Nitrite µg/filter	Std. Dev. µg/filter
1.	NaOH carried through extraction	3	0.40	0.07	0.02	0.01
2.	Lot 2075 filter	10	0.59	0.41	0.63	0.72
3.	Lot 2126 filter	10	0.58	0.17	0.62	0.26
4.	Lot 2203 filter	10	1.23	0.27	0.38	0.11
5.	August 19/82 field blanks	5	1.13	0.41	0.66	0.36
6.	Sept. 24/82 field blank	28	2.65	0.43	0.55	0.43

(i) n = number of samples
(ii) nitrate values are corrected for nitrite

A significant difference was found between lot 2203 filters and lots 2075 and 2125 filters. Similarly, even greater differences were noted between groups of field blanks. Thus optimal results would be obtained by keeping track of various lots in use and running a separate set of blanks for each lot. The current detection limit for nitrate on nylon filters is about 1 µg/filter compared to the original 4.8 µg/filter.

4.2.4 Sulphate on Impregnated Filters

No significant improvement was obtained in the detection limit for sulphate on impregnated filters as a result of changes in the analytical procedure. The major source of blanks and blank variance was the filter itself. Major improvements are possible only by changes in the filter quality. Because the impregnated filters are manufactured in-house by the Atmospheric Research Section, it was practical to institute a quality control system

for the filters. Filters are produced in batches of large sheets. Each sheet is sampled in three locations and these are analyzed. Sheets with an acceptably low sulphate concentration are then cut up into filters for use. The effectiveness of this quality control program has not yet been evaluated.

5.0 SUMMARY AND COMMENTS

5.1 The major limitation in the analysis of dichotomous sampler filters was shown to be contamination rather than the final method of determination. Thus ion chromatography would not show any advantage over continuous-flow analysis with respect to detection limit based on the present system. On the other hand, continuous flow analysis has a significantly greater sample throughput and lower analysis cost.

5.2 Contamination was substantially reduced, especially for nitrate, by a change in extraction container and filter materials.

5.3 The concentration of nitrite is significant at the lower concentrations of nitrate which can be determined after a reduction in contamination. Nitrite must therefore be determined separately in order to correct for its interference in nitrate determinations.

5.4 No significant lot-to-lot variation was observed for teflon filters but definite differences were noted for nylon filters. Thus all samples should be identified with respect to lot number and only blanks from the same lot should be used unless specific lots have been previously shown to be equivalent.

5.5 Twenty impregnated filters are cut from a single large sheet. Each sheet is subsampled at a minimum of three locations and these samples are analyzed for sulphate as a quality control measure. The remaining filters from a given sheet are only used if the sheet is declared acceptable.

5.6 The detection limit and variance for each analyte is determined from the blanks provided with each batch of samples rather than using a fixed detection limit determined at an earlier date. This is expected to provide more realistic analytical data because of the potentially large batch-to-batch variations.

5.7 Because the actual detection limits vary as noted in 5.6, the detection limits given in the report are actually average values.

Filter	Teflon			Nylon	Impregn.
Analyte	Sulphate	Nitrate	Ammonium	Nitrate	Sulphate
Original Detection Limit µg/filter	9.6	12	2	4.8	13
Current Detection Limit µg/filter	3	1	1	1	10

5.8 Sample handling has been organized to reduce analysis costs even though additional sample preparation is required. Because of continued changes in analytical requirements and reporting procedures, detailed cost comparisons are not possible between current procedures and the original methodology/1/. The only valid comparison is the cost of analyzing an entire filter pack (teflon, nylon and impregnated filters). The average current cost is $18.17 per pack including materials compared to an original cost of $24.90 per pack for a minimum batch size of 100 filter packs. This represents a reduction to 73% of the original cost.

6.0 ACKNOWLEDGEMENT

The technical work and documentation of the procedure was done by Mr. P. Agg.

Approved:

D. Harrison
Manager
Chemical Research Department

Submitted:

O. Herrmann
Chemist, Analytical Methods
Analytical Services Section

OH:km

REFERENCES

1. Herrmann, O. "Dichotomous-Sampler Filter Analysis". Ontario Hydro Research Division Report No 82-75-K.

2. Mehdi, S.H. "Ultrasonic Extraction of Aerosol Samples". Ontario Hydro Research Division Report No 80-183-K.

3. Massey, R.E. "Continuous-Flow Automated Ammonia Determination". Ontario Hydro Research Division Report No 80-414-H.

4. Massey, R.E. "Automated Nitrate and Sulphate Determinations". Ontario Hydro Research Division Report No 81-83-H.

APPENDIX A

ANALYTICAL PROCEDURE - DETERMINATION OF AMMONIA NITRATE, NITRITE AND SULPHATE IN TEFLON DICHOTOMOUS FILTERS

1.1 Equipment and Supplies

1.1.1 Technicon Autoanalyzer IIC system
1.1.2 Bransonic 72 ultrasonic bath
1.1.3 Millipore 12 port filtering manifold
1.1.4 Vacuum pump with trap
1.1.5 Sartorius 0.45 μm cellulose acetate filters
1.1.6 Sufficient Falcon tissue culture tubes for samples (1 each) - 15 mm x 125 mm - screw cap
1.1.7 Sufficient 25 mL glass vials for samples (1 each)
1.1.8 Sufficient 6 cm glass rods for samples (1 each)
1.1.9 Tweezers
1.1.10 Oxford Pipettor
1.1.11 Sufficient Technicon sample cups - 5 mL capacity
1.1.12 Magnetic stir plate
1.1.13 One 1.5 L beaker equipped with a watch glass and stir bar - calibrated for 500 mL and 1 L
1.1.14 1 50 mL pipette

1.2 Outline of Method

Each filter is immersed in 20 mL deionized water for 24 h and then the mixture is subjected to ultrasonic extraction for one-half hour. The extract is filtered and analyzed for NH_4^+, NO_3^-, NO_2^- and SO_4^{2-} using a Technicon Autoanalyzer II C system equipped with ammonia, nitrate and sulphate cartridges.

1.3 Interferences

1.3.1 A weak acid cation-exchange resin is used to overcome the interference of calcium, aluminum and iron in the sulphate chemistry. High levels of sodium and potassium interfere but are not generally a problem.

1.3.2 A high concentration of metal ions in the sample may interfere with the NO_3^- chemistry. This was not a problem with Teflon filters.

1.3.3 Calcium and magnesium ions may interfere with the NH_4^+ chemistry. This was not a problem with Teflon filters.

1.4 Concentration Range

Teflon filters containing 2 - 100 µg NH_4^+, 10 - 200 µg NO_3^- and 9 - 800 µg SO_4^{2-} can be analyzed easily without equipment modification. The upper limit of the ranges covers greater than 99% of the Teflon filters analyzed to date. More than 95% of the Teflon filters analyzed to date contain less than 10 µg NO_3^-.

1.5 Precision

The precision was defined as

$$\frac{2s}{\text{expected value}} \times 100$$

where 2s = twice the standard deviation of ten blank determinations spiked with a known analyte concentration.

expected value = the known analyte concentration.

The relative precision of the 1.0 mL eppendorf pipette used to make the standard addition was 1% (n=10), 2 s = 0.012, exp val = 0.974 mL.

1.5.1 Sulphate - 2.5 mg/L spike - 2s = 0.34
n = the number of samples = 10
relative precision = 4%

1.5.2 Nitrate - 1.4 mg/L spike - 2s = 0.20
n = 10
relative precision = 14%

- 9.4 mg/L spike - 2s = 0.20
n = 10
relative precision - 2%

1.5.3 Ammonia - 0.94 mg/L spike - 2s = 0.06
n = 10
relative precision - 6%

- 4.7 mg/L spike - 2s = 0.14
n = 10
relative precision - 3%

1.6 Reagents and Solutions

1.6.1 Alkaline Phenol (NH_4^+)	To a 1.5 L beaker containing 50 mL of deionized water add 83 g phenol and stir to dissolve. Cautiously add 180 mL of 10% sodium hydroxide in small increments with continuous agitation. Dilute the solution to 1 L and filter through glass fibre -C.
1.6.2 Complexing Reagent (NH_4^+)	To a 1.5 L beaker containing 950 mL deionized water add 33 g of potassium sodium tartrate and 24 g sodium citrate and stir to dissolve. Adjust the pH of this solution to 5.0 with concentrated sulphuric acid. Dilute the solution to 1 L and add 0.5 mL of Brij-35.
1.6.3 Sodium Hypochlorite (NH_4^+)	Dilute 200 mL of household bleach containing 5.25% available chlorine to 1 L with deionized wter.
1.6.4 Sodium Nitroprusside (NH_4^+)	To a 1.5 L beaker containing 900 mL of deionized water add 0.5 g of sodium nitroprusside. Stir to dissolve and dilute to 1 L.
1.6.5 Ammonium Chloride (NO_3^-)	Add enough ammonium hydroxide to 950 mL dionized water to attain pH 8.5. Add 10 g of ammonium chloride, stir to dissolve and dilute to 1 L. Add 0.5 mL of Brij-35.
1.6.6 Colour Reagent (NO_3^-)	To a 1.5 L beaker containing 400 mL deionized water, add 50 mL concentrated phosphoric acid and 5 g sulphanilamide. When dissolution is complete add 0.25 g of N-1-napthylethylene-diamine Dihydrochloride, stir to dissolve and dilute to 500 mL. Prepare monthly.

1.6.7	Hydrochloric Acid - 1N (NO_3^-)	
1.6.8	Copper Sulphate Stock Solution (NO_3^-)	Dissolve 2.0 g of $CuSo_4 \cdot 5H_2O$ in 50 mL deionized water and dilute to 100 mL.
1.6.9	Copper Sulphate Working Solution (NO_3^-)	Dilute 5 mL of copper sulphate stock solution to 50 mL.
1.6.10	Cadmium Metal, 30 to 60 mesh, granulated (NO_3^-)	
1.6.11	Bari um Chloride Solution (SO_4^{2-})	To a 1 L volumetric flask containing 500 mL deionized water add 1.4659 g $BaCl_2 \cdot 2H_2O$. Dissolve and dilute to 1 L.
1.6.12	Ethanol, C_2H_5OH - Absolute (SO_4^{2-})	
1.6.13	Hydrochloric Acid - 1N (SO_4^{2-})	
1.6.14	Alkaline EDTA Solution (SO_4^{2-})	To a 1.5 L beaker containing 600 mL deionized water add 6.75 g of ammonium chloride. When dissolution is complete add 57 mL ammonium hydroxide, stir, and dissolve 40 g of EDTA, tetrasodium salt. Dilute to 1 L and stir thoroughly.
1.6.15	Brij-35 Wetting Agent (SO_4^{2-}, NO_3^-, HN_4^+)	A 30% solution of Brij-35 is suitable for general use as a wetting agent in automated methods.
1.6.16	Ion Exchange Resin (SO_4^{2-})	This resin should be a weak cation exchange resin. Bio Res 70, sodium form, 20-50 mesh suitable.

1.6.17	Methylthymol Blue Solution, 0.006 M (SO_4^{2-})	To a 1 L volumetric flask add 50.0 mL of barium chloride solution (1.6.11) and dissolve 0.270 g of methylthymol blue in it. Add 8 mL of 1 M hydrochloric acid (1.6.13) and 142 mL of deionized water. Mix this solution for one half hour on a magnetic stirring plate. Add 0.5 mL Brij-35 solution and make the solution up to 1 L with absolute ethanol. Stir the solution thoroughly.
1.6.18	Sodium Hydroxide Solution - 0.18 N (SO_4^{2-})	To a 1.5 L beaker containing 900 mL of deionized water add 7.2 g of NaOH. Stir to dissolve and dilute to 1 L.
1.6.19	Stock Sulphate Solution 1000 mg SO_4^{2-} per litre	Dissolve 1.479 g of anhydrous $Na_2\ SO_4$ in 500 L deionized water and dilute to 1 L.
1.6.20	Stock Nitrate Solution 1000 mg NO_3^- per litre	Dissolve 1.631 g of anhydrous KNO_3 in 500 mL deionized water and dilute to 1 L. Preserve the nitrate with 2 mL chloroform per L.
1.6.21	Stock Ammonium Solution	Dissolve 3.662 g of anhydrous ammonium sulfate (dried at 100°C) in ammonia-free water and dilute to 1000 mL.
1.6.22	Stock Nitrite Solution 1000 mg NO_2^- per litre	Dissolve 1.4997 g sodium nitrite in 500 mL deionized water and dilute to 1 L. Preserve with 2 mL chloroform.
1.6.23	Working Sulphate-nitrate Standards	The volumes of 1000 mg/L sulphate and nitrate stocks shown below are added to 200 mL volumetric flasks and diluted to 200 mL with deionized water. Prepare daily.

A.	Sulphate (mg/L)	Nitrate (mg/L)	Sulphate Stock (mL)	Nitrate Stock (mL)
	7.5	5.0	1.5	1.0
	6.0	4.0	1.2	0.8
	4.0	3.0	0.8	0.6
	2.0	2.0	0.4	0.4
	1.0	1.0	0.2	0.2
	0.5	0.5	0.1	0.1

For example, mixed standard A (30.0 mg/L sulfate and 5.0 mg/L nitrate) is prepared by diluting a mixture of 6.0 mL sulfate stock plus 1.0 mL nitrate stock to 200 mL.

1.6.24 Working ammonium standards: 5.0, 4.0, 3.0, 2.0, 1.0 and 0.5 mg/L.

Add 1.0, 0.8, 0.6, 0.4, 0.2 and 0.1 mL of 1000 mg/L ammonium stock, respectively to separate 200 mL volumetric flasks and make up to volume with deionized water. Prepare daily.

1.6.25 Working nitrite standards: 2.0, 1.5, 1.0, 0.5 and 0.25 mg/L

Add 0.4, 0.3, 0.2, 0.1 and 0.05 mL of 1000 mg/L nitrite stock, respectively to separate 200 mL volumetric flasks and make up to volume with deionized water. Prepare daily.

1.7 Procedure

1.7.1 Sampling and Storage

Individual filters from the dichotomous filter pack are stored and transported in Falcon polystyrene petri dishes - 5 cm. Finger contact with the filter is avoided by using tweezers.

(a) The filters should not be handled roughly as this will dislodge particulates from the filter surface.

1.7.2 Sample Preparation

1.7.2.1 Each batch of filters to be analyzed is counted and separated according to filter type.

(b) If more than one batch of filters are to be analyzed, all the Teflon filters should be done together, then all the nylon filters, and then all the impregnated filters.

1.7.2.2 The Teflon filters are arranged on the bench top in an orderly manner.

1.7.2.3 The sample registry number of each batch of filters together with the sampling location and time periods covered are recorded.

1.7.2.4 The 25 mL glass vials are numbered and placed in 24-place Nalgene racks.

(c) The vials are rinsed twice with deionized water and are air dried in the clean room before use.

1.7.2.5 The filter type, sample origin, sample data and fraction designation (coarse or fine) are recorded beside a vial number for each filter.

1.7.2.6 With the aid of tweezers, each filter is inserted in its pre-designated vial.

(d) The filter should be handled using the polyolefin ring. Finger contact should be minimized.

1.7.2.7 20.0 mL of deionized water are added to each vial.

1.7.2.8 A glass rod is inserted in each vial to keep the filter completely immersed.

1.7.2.9 The vials are capped and allowed to sit for 24 h.

1.7.2.10 The vials are then subjected to ultrasonification for one half-hour.

(e) The Nalgene racks are supported in the ultrasonic bath two at a time.

1.7.2.11 The resulting solutions are filtered in groups of 12 using the Millipore 12 port filtering manifold equipped with 12 Sartonius 0.45 µm cellulose acetate filters. The filtrates are collected in Falcon tissue culture tubes - 15 mm x 125 mm. The solutions are now ready for analysis.

(f) The tissue culture tubes are not washed prior to use.

(g) Care must be taken to prevent the samples from becoming mixed-up at this point.

1.7.3 Instrument Set-Up

1.7.3.1 Turn on the following apparatus (i) sampler (ii) pumps (iii) colorimeter (iv) chart recorders (v) impact printer (vi) data handler. Plug in the NH_4^+ heating bath.

(a) Check to make sure there are sufficient reagents. If there are not, prepare them as described in 1.6.

1.7.3.2 Adjust the colorimeter conditions as follows.

SO_4 - Flow Cell - 50 mm x 2.0 mm ID

- Interference Filters - 460 nm

- Function - Operate

- Beam Select - Operate

- Chemistry Type - Direct

- Sample Holder - Flow Cell

- Damping - 2

- Standard Calibrate - Set such that highest standard reads 95 chart units.

NO_3 - Flow Cell - 15 mm x 2.0 ID

- Interference Filters - 520 mm

- Chemistry Type - Direct (D)

- Damping - Normal

- Standard Calibrate - Set such that highest standard reads 95 chart units.

NH_4 - Flow Cell - 50 mm x 2.0 ID

- Interference Filters - 630 mm

- Chemistry Type - Direct (D)

- Damping - Normal

- Standard Calibrate - Set such that highest standard reads 95 chart units.

1.7.3.3 Rinse and fill the two wash containers with deionized water.

(b) One wash container supplies deionized water to the sampler. The other supplies deionized water to the reagent lines.

1.7.3.4 Disconnect the cadmium reduction column on the nitrate cartridge and the weak cation exchange column on the sulfate cartridge.

(c) A new weak cation exchange column should be prepared after a full day's use. Wash the resin 3 times with deionized water before use.

1.7.3.5 Using a syringe and deionized water, force all the air bubbles from each column.

1.7.3.6 Position the platen on the pump and start the pump in order to draw deionized water through reagent lines.

(d) Paper towels should be placed under the fitting which was disconnected from the column.

1.7.3.7 After 3 minutes, reconnect the two columns, taking care to keep bubbles out.

1.7.3.8 Place the ammonium chloride line from the nitrate chemistry in 1N HCl for 1 minute. Return it to the deionized water for 1 minute.

1.7.3.9 Immerse each reagent line in the appropriate container.

1.7.3.10 When the baselines have stabilized, adjust each baseline to zero using the "baseline" control on the colorimeters.

(e) It may be necessary to pinch the pull-through line from the colorimeter flow-cell momentarily to remove bubbles.

1.7.4 Programming the Data Handler

Programming the "data handler" consists of responding to a series of messages from the "data handler". These messages, along with appropriate responses for running SO_4^{2-}, NO_3^- and NH_4^+ in Teflon filter extracts are outlined in detail below.

1.7.4.1

Message - "Command (Program, List, Math, Control, Run)"

Response - "Return"

(a) "Return" refers to hitting the "Return" key. The other components of the "Response" are typed in using the alphanumeric keyboard.

1.7.4.2

Message - "Reprogram/Modify"

Response - R, "Return"

(b) For programs which do not require major changes to the existing stored program "M" may be typed in instead of "R". The data handler then prints out each Message with the existing stored value printed after it in brackets. If a change in this stored value is not required the "Return" key is hit and the next message is printed.

1.7.4.3

Message - "Enter Tray Protocol"
"Cup No 2"

Response - 2N, 6C, H, 2L, 10s,
I, 10s, I, 10s, I,
5s, I, G, E,

(c) This response tells the data handler the order of calibration standards, intersample standards, carryover standards, gain standards and samples. The number before the letter tells how many of that type are successively placed in the tray. The tray protocol symbols shown in the above response represent the following:

Cup No 1 - The tray protocol always starts at Cup No 2. Cup No 1 is always a Primer. This is the highest calibrant and it signals the data handler that a run has begun. It must read between 50 and 100 chart units on the recorder.

2N - two null spaces in the tray protocol. Put deionized water in these cups.

6C - six different calibration standards of appropriate known concentration.

H,2L - one highest calibrant followed by two lowest calibrants. These are known as carryover standards.

10s - ten samples

I - one intersample standard. These play no part in the calibration process but are just treated as samples.

G - one gain standard. The response of this standard is compared to the response of a standard of equal concentration in the original six calibrants to correct for sensitivity drift.

E - Signals the end of the tray protocol.

1.7.4.4

Message - "Pause after cup #:"

Response - Return

(d) The sample tray holds 40 cups. When more than 40 cups are included in the tray protocol this message occurs. If no pause is desired, the response should be a number greater than the total number of cups in the tray protocol.

1.7.4.5

Message - "Gain Std Cup No"

Response - 8 Return

(e) This tells the data handler to compare the response of the gain standard to the response of the standard in cup No 8 and make the appropriate correction. This is usually the second highest calibrant.

1.7.4.6

Message - Statistics ?"

Response - N Return

(f) If the average and standard deviation of the samples and intersample standards are desired the response should be Y.

1.7.4.7

Message - "Sample/Hour

Response - 35 Return

(g) 1, 2, 3 or 4 channels may be used. The maximum number of tray positions per run are 160 with 1 channel, 80 with 2 channels, 53 with 3 channels, and 40 with 4 channels.

1.7.4.8

Message - "Sample/Hour

Response - 35 Return

(h) This response may be increased or decreased depending on the chemistry. In this case the SO_4^{2-} chemistry limits the number of samples per hour.

1.7.4.9

Message - "Sample/Wash Ratio"

Response - 2/1 Return

(i) This response implies that the sampler probe spends two times as much time in sample as it does in wash.

1.7.4.10

Message - "Flag Errors"

Response - Y Return

1.7.4.11

Message - Channel Parameters
Channel 1
Name of Chemistry:

Response - SO_4 Return

1.7.4.12

Message - Calibration Concentrations: Base
Response - 0 Return

Message - 1
Response - 10 return

Message - 2
Response - 20 return

Message - 3
Response - 40 return

Message - 4
Response - 80 return

Message - 5
Response - 120 return

Message - 6
Response - 150 return

Message - Units
Response - µg/Filt. Return

(j) These responses tell the computer the equivalent concentrations of the calibrants for the analyte assigned to channel 1. These values are expressed as "µg/filter". Since the samples are extracted in 20 mL of H_2O, a value of an analyte concentration given in "µg/mL" would have to be multiplied by 20 to give "µg/filter". Multiplying the actual concentration value of each calibrant by 20 achieves the same result.

1.7.4.13

Message - High-Low Limits?

Response - N Return

Message - Calibration Curve (linear, Nonlinear, Piecewise)

Response - P Return

(k) The sulfate chemistry is not linear. A piecewise calibration curve gives the most accurate results.

1.7.4.14

Message - Chemistry Inverse?

Response - N Return

1.7.4.15

Message - Carryover Correction (%)?

Response - Return

1.7.4.16

Message - Noise Tolerance (%)

Response - 0.9 Return

(1) This is the maximum noise tolerance possible.

1.7.4.17

Message - Channel 2
Name of Chemistry

Response - NO^3 Return

1.7.4.18

Message - Calibration
Concentrations
Base

Response - 0 Return

Message - 1
Response - 10 Return

Message - 2
Response - 20 return

Message - 3
Response - 40 return

Message - 4
Response - 60 return

Message - 5
Response - 80 return

Message - 6
Response - 100 return

Message - Units
Response - µg/Filt. Return.

1.7.4.19

Message - High-Low Limits?

Response - N Return

1.7.4.20

Message - Calibration Curve
(Linear, Nonlinear,
Piecewise)

Response - L Return

1.7.4.21

Message - Chemistry Inverse?

Response - N Return

1.7.4.22

Message - Carryover Correction
(%)

Response - Return

1.7.4.23

Message - Noise Tolerance (%)

Response - 0.9 Return

1.7.4.24

Message - Channel 3
Name of Chemistry

Response - NH_4

1.7.4.25

Message - Calibration
Concentrations: Base

Response - 0 Return

Message - 1
Response - 10 return

Message - 2
Response - 20 return

Message - 3
Response - 40 return

Message - 4
Response - 60 return

Message - 5
Response - 80 return

Message - 6
Response - 100 return

Message - Units
Response - µg/Filt.

1.7.4.26

Message - High-Low Limits?

Response - N Return

1.7.4.27

Message - Calibration Curve
(Linear, Nonlinear,
Piecewise)

Response - L Return

1.7.4.28

Message - Chemistry Inverse?

Response - N Return

1.7.4.29

Message - Carryover
Correction (%)

Response - Return

1.7.4.30

Message - Noise Tolerance (%)

Response - 0.9 Return

1.7.4.31

Message - Autovalve 1 Sequence
Enter (Minutes After
Last Data) or 'N' if
not Req'd. Wash Valve
- Wash:

Response - These 10 messages
regarding the auto-
valve sequences
should be responded
to with N Return

1.7.4.32

Message - Command (Program,
List, Math, Control,
Run)

Response - R Return

1.7.4.33

Message - Warning - Wash Valve
Wash
Warning - Wash Valve
Wash
Automatic Shutdown?

Response - N Return

1.7.4.34

Message - Operator

Response - "your initials"
Return

1.7.4.35

Message - Date

Response - "today's date"
Return

1.7.4.36

Message - First Sample ID No: (1)

Response - 1 Return

(m) This sample ID number is not applicable unless the samples are numbered sequentially.

1.7.4.37

Message - Enter Active Channel Numbers:

Response - 1, 2, 3 Return

1.7.4.38

Message - To Start Run, Type "Ctrl R"

(n) At this point, the data handler is programmed and ready for operation.

1.7.5 Analysis of the Extracts

1.7.5.1 With the recorder baselines reading zero, immerse the NH_4^+ sampler probe in the 5.0 mg/L standard NH_4^+ solution for 1 minute. Immerse the SO_4^{2-}, NO_3^- sampler probe in the 7.5 mg/L SO_4^{2-} - 5.0 mg/L NO_3 standard for 1 minute.

(a) The highest standard of each analyte is referred to as the full scale standard.

1.7.5.2 When the coloured analyte complex has reached the flowcell and the recorder has reached it's maximum steady state value adjust the "standard calibrate" control to give a 95 chart unit reading on the recorder. Do this for each chemistry.

1.7.5.3 Fill the 5 mL cups with standard and samples and place them in the sampler tray according to the tray protocol given in 1.7.4.3.

(b) The run may be started after the six calibrants have been placed in the tray. Record the order and identification of all standards and samples.

1.7.5.4 When the baselines are constant and at least six calibrants have been added to the tray the run can be initiated by pressing the "CTRL" key and the "R" key simultaneously.

1.7.5.5 The "baseline accept" can then be overridden by pressing the "CRTL" key and the "B" key simultaneously. This should start the sampler.

1.7.5.6 The filling of the sampler tray can then be completed.

(c) Include a nitrite standard as one of the intersample standards.

(d) As each sample is processed a "real time" concentration value is printed out. These values are uncorrected. When the run is completed, a second set of data is printed out. These concentration values are corrected for sensitivity drift, baseline drift and carryover.

1.7.5.7 Using the value obtained for the nitrite standard with the column in place, calculate a correction factor and correct all nitrate values for the nitrite content.

(e) If $a = [NO_2^-]$ in a standard run with nitrate samples (Cd column in place) and $b = [NO_3^-]$ obtained for that sample, then each nitrite value must be multiplied by b/a before correcting the nitrate values for nitrite.

Average the blank values for each analyte and subtract this from the concentration values obtained for each sample. Report these results for SO_4^{2-}, NO_3^-, NO_2^-, and NH_4^+ in µg/filter.

1.7.5.8 Another run may now be initiated or the instrument may be shut down as follows:

1.7.5.9 Remove all reagent lines from the solutions and immerse them in deionized water for 20 minutes.

1.7.5.10 Turn off the following apparatus (i) sampler (ii) colorimeter (iii) chart recorder (iv) impact printer (v) data handler. Unplug the NH_4^+ heating bath.

1.7.5.11 Remove the pump platen and turn off the pump power.

ANALYTICAL PROCEDURE - DETERMINATION OF NITRATE AND NITRITE IN NYLON DICHOTOMOUS FILTERS

2.1 Equipment and Supplies - Same as 1.1

2.2 Outline of Method

Each filter is immersed in 20 mL of 0.003 N NaOH for 24 h and then the mixture is subjectd to ultrasonic extraction for one-half hour. The extract is filtered and analyzed for NO_3^- and NO_2^- using a Technicon Autoanalyzer II C system equipped with a nitrate cartridge.

2.3 Interference

2.3.1 A high concentration of metal ions in the sample may interfere with the NO_3^- chemistry. This was not a problem with nylon filters.

2.4 Concentration Range

Nylon filters containing 1 - 200 µg NO_3^- and 1 - 200 µg NO_2^- can be analyzed easily without equipment modifications.

2.5 Precision - Nitrate - 0.94 mg/L spike, 2s = 0.34
n = the number of samples = 10
relative precision = 36%

- 6.6 mg/L spike, 2s = 0.70
n = 10
relative precision = 11%

2.6 Reagents and Solutions

2.6.1 The necessary reagents and methods for their preparation are described in 1.6.5 - 1.6.10.	In addition, 20 mL of 0.003 N NaOH are needed for each sample.
2.6.2 Sodium hydroxide, 0.003 N	Add 6.0 mL of 1 N NaOH to a 2 L volumetric flask and dilute to 2 L with deionized water.

2.6.3	Stock Nitrate Solution 1000 mg NO_3^- per litre	Dissolve 1.361 g of anhydrous KNO_3 in 500 mL deionized water and dilute to 1 L. Preserve the nitrate with 2 mL chloroform per L.
2.6.4	Stock Nitrite Solution 1000 mg NO_2^- per litre	Dissolve 1.4997 g sodium nitrite in 500 mL deionized water and dilute to 1 L. Preserve with 2 mL chloroform.
2.6.5	Working Nitrate Standards 5.0, 2.5 and 1.0 mg/L Nitrate	Add 1.0, 0.5 and 0.2 mL of 1000 mg/L stock nitrate solutions respectively to 200 mL volumetric flasks and dilute to 200 mL with deionized water.
2.6.6	Working Nitrite Standards 2.0, 1.0 and 0.5 mg/L nitrite.	Dilute 0.4, 0.2 and 0.1 mL stock nitrite (1000 mg/L) solution to 200 mL with deionized water.

2.7 Procedure

The procedure outlined in 1.7 should be followed, ignoring references to the $SO_4^=$ and NH_4^+ chemistries. The only changes involve the extracting solution, tray protocol, number of channels, samples per hour, channel number of the nitrate chemistry and number of concentrations of calibrants. These changes are outlined in detail to the right. Run nitrite in the same manner as nitrate except that the Cd reduction column is removed and nitrite standards are used. Sampling rate is 70 per hour.

(a) The deionized water referred to in 1.7, 2.7 is changed to 0.00300 NaOH for nylon filters.

(b) The tray protocol of 1.7.4.3 is changed to 3C,H,2L,10s,I,10s,I,10s,I,10s,I,10s,I,10s,I,10s,I,G,E. The capacity of the date handler is increased to 160 cups with only one chemistry, but 70 samples per run is a practical number.

(c) The response in 7.4.7 is changed to "1".

(d) Delete 1.7.2.8.

(e) The "response" in 1.7.4.8 is changed to 70.

(f) Ignore the responses in 1.7.4.11 - 1.7.4.16 and 1.7.4.24 - 1.7.4.30 and substitute the responses in 1.7.4.17 - 1.7.4.23 for the messages starting in 1.7.4.11 "Channel 1 Name of Chemistry". Use the new calibrant values of 100, 50 and 20 µg/filter. This simply programs the parameters for nitrate in Channel 1.

(g) The response in 1.7.4.37 is changed to "1" Return.

ANALYTICAL PROCEDURE - DETERMINATION OF SULFATE IN K_2CO_3 IMPREGNATED W41 DICHOTOMOUS FILTERS

3.1 Equipment and Supplies - Same as 1.1.

3.2 Outline of Method

Each filter is immersed in a 0.002 N HCl - 0.6 g/L (0.06%) H_2O_2 for 24 h and then the mixture is subjected to ultrasonic extraction for one-half hour. One gram of strong cation exchange resin is added to remove potassium and other cationic interferants. The extract is filtered and analyzed for sulfate using a Technicon Autoanalyzer II C system equipped with a sulfate cartridge.

3.3.1 The addition of the strong cation exchange resin removes cationic interferences such as calcium, sodium, potassium aluminum and iron.

3.4 Concentration Range

Impregnated filters containing 10 - 800 µg of SO_4^{2-} can be analyzed easily without equipment modification. The non-linearity of the sulfate chemistry is responsible for significant errors in the analysis of filters containing greater than 800 µg SO_4^{2-}.

3.5 Precision - Sulfate - 4.6 mg/L spike, 2s = 0.36
n = 8
relative precision = 8%

- 23.2 mg/L spike, 2s = 0.66
n = 8
relative precision = 3%

- 34.8 mg/L spike, 2s = 0.48
relative precision = 1%

3.6 Reagents and Solutions

3.6.1	The necessary reagents and methods for their preparation are described in 1.6.11 - 1.6.18	In addition, 20 mL of a 0.002 N HCl; - 0.6 g/L H_2O_2 solution are needed for each sample.
3.6.2	Extractant 0.002 N HCl, 0.06% H_2O_2	Add 4 mL of 1 N HCl, and 4 mL of 300 g/L H_2O_2 to a 2 L volumetric flask and make up to volume with deionized water.

3.6.3	Strong cation-exchange resin	Amberlite 1R-120(H) or equivalent analytical grade sulphonic acid resin is suitable. Soak a batch of several hundred grams in 1 N HCl for one hour. Rinse with deionized water. Repeat twice. Store in 0.1 N HCl until ready for use. When needed, wash sufficient resin (1 g per sample) in deionized water until the washings are not acidic.
3.6.4	Working sulfate standards 40, 35, 30, 20, 10, 5, 3, 1 mg/L	The maximum number of standards possible with the autoanalyzer and the piecewise calibration are required because of the non-linear calibration curve. Add 8.0, 7.0, 6.0, 4.0, 2.0, 1.0, 0.6 and 0.2 mL of 1000 mg/L stock solution to 200 mL volumetric flasks and make up with deionized water. Prepare daily.

3.7 Procedure

The procedure outlined in 1.7 should be followed, ignoring references to the nitrate and sulfate chemistries. Changes involve column removal, extracting solution resin addition, tray protocol, number of channels and calibrants. Details of these changes are given below.

3.7.1	Change the deionized water extractant in 1.7.2.7 to 0.002 N HCl - 0.6 g/L H_2O_2 solution
3.7.2	Delete 1.7.2.8
3.7.3	After 1.7.2.10, 1 g of acid-washed resin (3.6.3) is added to each sample and the bottles are swirled occasionally over a 3-h period.
3.7.4	Delete 1.7.3.3 - 1.7.3.7

3.7.5 Remove the weak cation-exchange resin column and replace it with a polyethylene tube.

3.7.6 Change the response in 1.7.4.3 to:
8C,H,2L,10s,I,10s,I,
10s,I,10s,I,10s,I,10s
10s,I,G,E.

3.7.7 Change the response in 1.7.4.7 to "1 Return".

3.7.8 Type in appropriate values for the 8 calibrants in 1.7.4.12.

3.7.9 Delete 1.7.4.17 - 1.7.4.30

3.7.10 Change response in 1.7.4.37 to 1 Return".

POOR

QUALITY

ORIGINAL